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A continuum-approach modelling of surface composition and ternary component distribution inside low fat milk emulsions during single droplet drying

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Abstract

Surface composition of dairy powders plays an important role in determining the functionality. However, the surface composition may be different from the bulk composition because of component migration during drying. In this study, a comprehensive mathematical model has been developed to describe the phenomena. To the best of our knowledge, it is the first mathematical model which predicts the dynamics of surface composition during drying. The model consists of a set of equations of conservation of mass of water, lactose, protein and fat as well as conservation of heat and momentum in which the effects of diffusion induced material migration (DIMM) and surface activity are incorporated. This model is applicable to describe the kinetics of surface composition of dairy droplets during drying. It suggests that both diffusion and protein surface activity govern the component segregation during drying. The study indicates that the model implementing the measured initial surface composition as the initial conditions generates more realistic profiles than the one using the bulk composition.

The modelling confirms that the difference between the surface and bulk composition that occurs prior to drying is not primarily governed by diffusion, but the emulsion's atomization behaviour seems to play an essential role in the overrepresentation of fat.

Key words: model, component segregation, drying, surface composition, heat and mass transfer, milk emulsion

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1. Introduction

Spray drying is still considered the most effective method to produce dairy powders. It is also commonly implemented in food industry for encapsulation of heat sensitive materials. During spray drying, the liquid is atomized and contacted intensively with a hot air stream to remove the moisture followed up by separation of air and particles in a cyclone¹. Both efficiency and powder functionality are essential in the spray drying operation. The powder functionality is important since it influences particle's wettability, flowability and dissolution kinetics. The presence of fat at the surface tends to increase the susceptibility to oxidation and may reduce flowability². In order to modify the dissolution behaviour of powders containing high fat content, surfactants are commonly applied to lower the air/water barrier. The solubility is further affected by the state of protein as influenced by pH and temperature³. Sticky particles due to fat coverage will reduce the manufacturing efficiency because of wall deposition which may lead to product loss, spontaneous combustion and product contamination. The sticky particles will also adversely affect powder handling and distribution to consumers³.

The microstructure at the surface of a particle is one key link between processing parameters and product properties. The surface composition, governed by transport of species inside the particles, provides essential information on relationships between the drying parameters and powder functionality^{4,5}. Interestingly, the discrepancy between the bulk and surface composition in milk powder is typically significant and affected by the drying conditions⁶⁻⁸. Skim milk powders with a bulk composition of 58% lactose, 41% protein and 1% fat had a surface composition of 36% lactose, 46% protein and 18% fat⁹. For the whole milk powders with bulk composition of 40% of lactose, 31% of protein and 29% of fat, 98% of the surface was covered by fat⁹. It indicates that solute segregation occurs during drying of dairy droplets.

Although the understanding of transport of the species inside the droplets is useful to determine the powder surface properties, the transport mechanisms are still unclear¹⁰. The component migration may be governed by particle formation, diffusion and protein adsorption at the air/water interface⁹. Droplets containing high fat tend to yield early shell formation along with wrinkle morphology which inhibit the water ingress. This may result in the significant fat coverage¹¹. During drying, the surface water evaporation forms a radial gradient in water concentration accompanied by diffusion in the opposite direction towards the droplet centre. The diffusion of each component is governed by its diffusivity as affected by the molecular size. Since fat globules had the largest size, overrepresentation of fat at the surface was expected¹². Protein may be transported to the surface during drying due to its surface activity. The decrease of surface tension at the air/water interface may be observed along with significant coverage of protein at the surface¹³. In addition, the difference between bulk and surface composition may be triggered by the disintegration behaviour of the emulsions during droplet generation or atomization. It seems that the presence of fat at the surface of milk

particles is enhanced by the atomization. Although the droplets contained very low concentration of fat, the concentration of fat at the particle surfaces was significant, which was explained by the break-up behaviour of the fat globules containing milk emulsions⁶⁻⁸. In line with this, the overrepresentation of surface composition of fat in the corresponding atomized droplets was shown¹⁴⁻¹⁵. When single droplet drying was implemented, similar phenomena were also observed¹⁶.

In industrial settings, several attempts have been made to adjust the drying conditions to modify the surface composition. The efforts were basically aimed at quenching the system. If the drying kinetics were faster relative to the transport velocities in the droplets, the component migration was retarded⁷. The high drying temperatures were useful to reduce the solute migration due to enhanced drying rate which facilitated the formation of a solid structure¹⁷. Similar effects were also demonstrated by increasing the feed concentration which increased the viscosity of the droplets. While the droplet size played an important role in the component segregation of skim milk powders, the effects on whole milk powders were not significant. Homogenization of the concentrate after fat addition helped to reduce the overrepresentation of fat at the surface⁷. For studying the kinetics of surface properties during drying, complex procedures are required. On top of continuously recording the sample mass, diameter and temperature, the surface composition of lactose, protein and fat need to be constantly measured. For this purpose, the drying experiments need to be stopped at certain interval of time by flash freezing followed up by freeze drying and measurement of the component surface distribution using X-ray photoelectron spectroscopy. In industrial settings, the procedures seem not to be practical and the instruments may not be available. Therefore, predictive tools are useful for monitoring the kinetics of surface composition during drying.

Mathematical modelling is a useful tool to effectively fine-tune the drying conditions to produce food and pharmaceutical powders with the tunable properties. The understanding of surface composition and surface temperature is essential to accurately estimate the glass transition temperature (T_g), which yields rationale basis to project the flowability properties and stickiness of food and pharmaceutical powders. Similarly, through the information of surface composition and distribution of components inside the powders, the dissolution profiles can be better approximated. There has been a significant number of studies focusing on modelling the moisture content and temperature inside the droplets during drying¹⁸⁻²². Generally, they implemented a generic diffusion model coupled with a heat balance to represent the dynamics of moisture content and temperature^{18, 20, 23}. The reaction engineering approach (REA) was applied to describe the drying kinetics of several formulations of dairy droplets^{19, 24}. The spatial reaction engineering approach (S-REA) was further implemented to describe several challenging cases of heat and mass transfer²⁵⁻²⁹. Although surface composition plays a vital role in determining the powder functionality, only a few modelling studies have been attempted to predict the surface composition. An analytical expression based on diffusion equations has been developed to represent the final surface composition of dairy powders³⁰. The simulation resulted in simple algebraic equations with good agreement towards the experimental data. The approach was then implemented to model the surface composition of casein in a binary system of casein and lactose³¹. The model was further extended to include the microscale packing model with good agreement towards the experimental data of the binary system³².

The above models of solute segregation are potentially able to capture the final surface composition of dairy powders. Nevertheless, to the best of our knowledge, there is no model which predicts the dynamics of surface composition during drying along with the

spatiotemporal profiles inside the materials. These predictions will be useful to analyse the transport phenomena inside the materials undergoing heat and mass transfer. The predicted surface properties can then be used to better estimate the stickiness, flowability and dissolution behaviours of dairy powders. By embedding with the equations of conservation of drying air inside spray dryer, the model can serve as an alternative tool in optimising the drying schemes to engineer dairy powders with desirable properties.

This study aimed at developing a mathematical model which predicts the dynamics of surface composition as well as transport phenomena inside dairy droplets containing low fat content during drying. A heat and mass transfer model was developed and coupled with a set of equations of mass conservation of lactose, protein and fat. Both diffusion and protein surface activity were taken into account. Semi-empirical shrinkage and evaporation resistance models were implemented by means of REA to realistically describe the influence of crust formation. The simulated results were benchmarked towards the published experimental data about the surface composition after discrete drying times.

2. Review of experimental details

The experimental data used for validation of this study was derived from the previous work¹⁶. For better understanding of the modelling framework, the experimental details are briefly reviewed here. A model of milk emulsion whose composition is listed in Table 1 was prepared. By using a micro-volume syringe, droplets of 1-3 μl in volume were generated and suspended at the tip of a thin glass filament. Standard single droplet drying, whose details have been presented previously^{24, 33}, was carried out to determine the drying and shrinkage characteristics. A controlled drying air stream at a drying air temperature of 70 °C, a velocity of 0.75 m.s^{-1} and a humidity of 0.0001 kg water/kg dry air was fed into the drying chamber. In

addition, at certain drying times (0, 20, 50, 100 and 200s), the drying process of 3 µl droplets was stopped instantly by flash-freezing with liquid nitrogen. This was followed by freeze-drying of the droplets and measurement of the component surface distribution using X-ray photoelectron spectroscopy.

3. Mathematical modelling

In this study, a set of equations of conservation of heat and momentum transfer was combined with a set of equations of mass conservation of lactose, protein and fat to estimate the component distribution inside the droplet during drying. For modelling water removal from the droplet during drying, the mass balance of water can be represented as²⁵:

$$\frac{\partial(C_s X)}{\partial t} = \frac{1}{r^2} \left(\frac{\partial}{\partial r} \left(D_w r^2 \frac{\partial(C_s X)}{\partial r} \right) \right) \quad (1)$$

where X is the concentration of liquid water [kg H₂O/kg dry solids], D_w is the capillary diffusivity [m²/s], C_s is the solids concentration [kg dry solids/m³], t is the time [s] and r is the radial position [m].

The heat balance can be written as²⁵:

$$\rho C_p \left(\frac{\partial T}{\partial t} + v_r \frac{\partial T}{\partial r} \right) = \frac{1}{r^2} \left(\frac{\partial}{\partial r} \left(k r^2 \frac{dT}{dr} \right) \right) \quad (2)$$

Where T is the droplet temperature [K], k is the thermal conductivity [W/m/K], v_r is the shrinkage velocity of the droplet [m/s], C_p is the droplet specific heat [J.kg/K] and ρ is the droplet density [kg/m³].

The momentum balance can be expressed as:

$$\rho \left(\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} \right) = \mu \left(\frac{\partial}{\partial r} \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 v_r) \right) \quad (3)$$

where μ is the dynamic droplet viscosity [Pa·s].

The initial and boundary conditions for equations (1) to (3) are:

$$t=0, \quad X = X_0 \quad (\text{initial condition})$$

$$T = T_0 \quad (\text{initial condition})$$

$$v_r = v_0 \quad (\text{initial condition}) \quad (4)$$

$$r=0, \quad \frac{dX}{dr} = 0 \quad (\text{symmetry})$$

$$\frac{dT}{dr} = 0 \quad (\text{symmetry})$$

$$v_r = 0 \quad (\text{zero radial velocity}) \quad (5)$$

$$r=R, \quad -C_s D_w \frac{dX}{dr} = h_m (\rho_{v,s} - \rho_{v,b}) \quad (\text{convective boundary of mass transfer})$$

$$k \frac{dT}{dr} = h(T_b - T) - h_m (\rho_{v,s} - \rho_{v,b}) \Delta H_{vap} \quad (\text{convective boundary of heat transfer})$$

$$v_r = v_s \quad (\text{shrinking velocity}) \quad (6)$$

where h_m is the mass transfer coefficient [m/s], h is the heat transfer coefficient [W/m²/K], $\rho_{v,s}$ is the surface water vapor concentration [kg/m³], $\rho_{v,b}$ is the drying air water vapor concentration [kg/m³], T_b is the drying air temperature [K] and v_s is the shrinking velocity [m/s] and R is the droplet radius [m].

The reaction engineering approach (REA) was used in equation (6) to serve as the convective boundary of mass and heat transfer. As drying progressed, the surface relative humidity decreased during drying so that the surface water vapor concentration ($\rho_{v,s}$) was lower than the saturated water vapor concentration ($\rho_{v,sat}$). The relationship between surface and saturated water vapour concentration can be expressed as:

$$\rho_{v,s} = \psi_s(X, T) \rho_{v,sat} \quad (7)$$

where ψ_s is the surface relative humidity dependent on moisture content (X) and temperature (T).

By using the REA (reaction engineering approach), the surface water vapour concentration ($\rho_{v,s}$) can be expressed as^{34,35}:

$$\rho_{v,s} = \exp\left(\frac{-\Delta E_v(X)}{RT}\right) \rho_{v,sat} \quad (8)$$

where T is the temperature [K] and ΔE_v is the activation energy [J/mol] dependent on the moisture content. The activation energy (ΔE_v) essentially described the difficulty to remove the moisture from the materials being dried. The dependency of the activation energy on the moisture content was expressed using the relative activation energy function ($\Delta E_v/\Delta E_{v,b}$). The coupling of the equilibrium activation energy ($\Delta E_{v,b}$) with the relative activation energy ($\Delta E_v/\Delta E_{v,b}$) resulted in unique relationships of activation energy (ΔE_v) which represented the changes of internal material structure during drying as affected by the drying conditions. The relative activation energy ($\Delta E_v/\Delta E_{v,b}$) was material specific but independent on the drying conditions^{34,35}. The relative activation energy was zero at the beginning of drying and achieved one when the equilibrium conditions were attained. Therefore, by using the REA, the boundary condition of mass transfer at $r=R$, represented in equation (6), can be expressed as:

$$-C_s D_w \frac{dX}{dr} = h_m \left[\exp\left(\frac{-\Delta E_v(X)}{RT}\right) \rho_{v,sat} - \rho_{v,b} \right] \quad (9)$$

while that of heat transfer, represented in equation (6), can be written as:

$$k \frac{dT}{dr} = h(T_b - T) - h_m \left[\exp\left(\frac{-\Delta E_v(X)}{RT}\right) \rho_{v,sat} - \rho_{v,b} \right] \Delta H_{vap} \quad (10)$$

For low fat milk emulsion (LFME) droplets, the relative activation energy ($\Delta E_v/\Delta E_{v,b}$) can be expressed as:

$$\begin{aligned} \frac{\Delta E_v}{\Delta E_{v,b}} = & 0.006(X - X_b)^6 - 0.0917(X - X_b)^5 + 0.5618(X - X_b)^4 \\ & - 1.7371(X - X_b)^3 + 2.8473(X - X_b)^2 - 2.4349(X - X_b) \\ & + 1.027 \end{aligned} \quad (11)$$

The relative activation energy was generated from experiments of drying of 2 μ l LFME droplets at a drying air temperature of 70 °C. Since the relative activation energy of the same materials is independent from the drying conditions³⁵, equation (11) was used to describe the drying of 3 μ l LFME droplets at a drying air temperature of 70 °C. In addition, as it was found that perfect shrinkage is not applicable for the investigated emulsion¹⁵, a more realistic description of droplet shrinkage during drying was also incorporated by means of the experimentally derived single droplet drying data, as presented in Appendix (equation (A2)).

For predicting the surface composition and distribution of concentration of lactose (C_l), protein (C_p) and fat (C_f) during single droplet drying, the mass balance of water (equation (1)), heat balance (equation (2)) and momentum balance (equation (3)) were combined seamlessly with the mass balance of lactose, protein and fat as shown in equations (12), (13) and (14), respectively.

The mass balance of lactose could be expressed as:

$$\frac{\partial C_l}{\partial t} + v_r \frac{\partial C_l}{\partial r} = \frac{1}{r^2} \left(\frac{\partial}{\partial r} \left(D_l r^2 \frac{\partial C_l}{\partial r} \right) \right) \quad (12)$$

where C_l is the concentration of lactose [kg/m^3] and D_l is the diffusivity of lactose [m^2/s].

The mass balance of protein can be written as:

$$\frac{\partial C_p}{\partial t} + v_r \frac{\partial C_p}{\partial r} = \frac{1}{r^2} \left(\frac{\partial}{\partial r} \left(D_p r^2 \frac{\partial C_p}{\partial r} \right) \right) \quad (13)$$

where C_p is the concentration of protein [kg/m³] and D_p is the diffusivity of protein [m²/s].

The mass balance of fat can be represented as:

$$\frac{\partial C_f}{\partial t} + v_r \frac{\partial C_f}{\partial r} = \frac{1}{r^2} \left(\frac{\partial}{\partial r} \left(D_f r^2 \frac{\partial C_f}{\partial r} \right) \right) \quad (14)$$

where C_f is the concentration of fat [kg/m³] and D_f is the diffusivity of fat [m²/s].

The initial and boundary conditions of equations (12) to (14) were:

$$\begin{aligned} t=0, \quad C_l &= C_{l0} && \text{(initial condition)} \\ C_p &= C_{p0} && \text{(initial condition)} \\ C_f &= C_{f0} && \text{(initial condition)} \end{aligned} \quad (15)$$

$$\begin{aligned} r=0, \quad \frac{dC_l}{dr} &= 0 && \text{(symmetry)} \\ \frac{dC_p}{dr} &= 0 && \text{(symmetry)} \\ \frac{dC_f}{dr} &= 0 && \text{(symmetry)} \end{aligned} \quad (16)$$

$$\begin{aligned} r=R, \quad D_l \frac{dC_l}{dr} &= C_l v_s && \text{(no flux)} \\ D_p \frac{dC_p}{dr} &= k_p C_p - k_d q && \text{(adsorption at interface)} \\ D_f \frac{dC_l}{dr} &= C_f v_s && \text{(no flux)} \end{aligned} \quad (17)$$

where k_p is the adsorption kinetic parameters [m/s], k_d is the desorption kinetic parameters [1/s] and q is the concentration of protein at the adsorbed layer [kg/m²].

In this study, the spatial profiles of moisture content (X), temperature (T), radial velocity (v_r), concentration of lactose (C_l), protein (C_p) and fat (C_f) during single droplet drying were generated. For this purpose, the mass balance of water (equation (1)), heat balance (equation (2)), momentum balance (equation (3)), mass balance of lactose (equation (12)), mass balance of protein (equation (13)) and mass balance of fat (equation (14)) were solved simultaneously in conjunction with the initial and boundary conditions shown in equations (4) to (6) as well as equations (15) to (17). Method of lines was implemented to solve these equations simultaneously. In this way, the partial differential equations were transformed into a set of ordinary differential equations with respect to time by firstly discretizing the spatial derivatives. The ordinary differential equations were then solved simultaneously numerically by ordinary differential solver *ode23s* in Matlab® that implemented Rosenbrock formula of order 2. The numerical solutions resulted in the spatial profiles of moisture content (X), temperature (T), radial velocity (v_r), concentration of lactose (C_l), protein (C_p) and fat (C_f) inside the droplets during single droplet drying. The surface composition of lactose (C_l), protein (C_p) and fat (C_f) were determined based on the predictions of these concentrations at the outermost layer. The procedures to determine the diffusivities of lactose, protein and fat along with the kinetic parameters are presented in Appendix.

Two different initial conditions for the surface composition were compared in this study. Firstly, the experimentally measured surface composition of lactose, protein and fat (listed in Table 1) was implemented (equation (15)). The initial condition of the remaining part of the droplet was calculated based on conservation of mass. Secondly, the bulk compositions of lactose, protein and fat were applied as the initial surface condition (equation (15)).

4. Results and Discussion

4.1. Modelling of the component segregation during single droplet drying using the measured surface composition as initial condition (scheme 1)

For scheme 1 (experimentally determined surface composition as initial condition), the results of modelling of component segregation using equations (1) to (17) are presented in Figures (1) to (5). Figures 1(a) and 1(b) describe the temporal profiles of average moisture content and surface temperature during drying. As shown in Figures 1(a) and 1(b), the results of modelling match well with the experimental data. The good agreement is indicated by R^2 of 0.998 for both moisture content and temperature profiles. The model seems to be accurate to model both moisture content and temperature during drying.

The spatial profiles of moisture content and temperature are shown in Figures S1 and S2 (supplementary figure files). Figure S1 indicates that the moisture content at the outer part was lower than that at the inner part of the droplets. This means that the moisture migrated outwards during drying since the surface water vapor concentration at the surface was higher than the concentration at the surrounding medium. Initially, the gradient of moisture content during drying was relatively large. However, this decreased as drying progressed in line with the depletion of moisture inside the droplets during drying. At the end of drying, the gradient was not noticeable which indicated that the equilibrium condition was nearly attained. Similar profiles were also observed during drying modelled using the spatial reaction engineering approach (S-REA)^{25, 28, 34}. For the temperature profiles, as shown in Figure S2, there was no noticeable gradient of temperature during drying. This was in agreement with the Ch_Bi ³⁶ of less than 0.01 which indicated that the temperature inside the droplets was essentially uniform. Previous studies also indicated that the temperature inside the samples were basically uniform^{25,}

Figure 2(a) indicates a reasonable agreement between the predicted and experimental surface composition of lactose if the experimentally derived initial surface composition was applied as initial condition. The model estimated well the trend of kinetics of surface composition of lactose during drying. The reported composition refers to the concentration of the component excluding water. As shown in Figure 3, during drying, the composition of lactose at the outer part of the droplets was lower than that at the core of samples. This seems to be resulted by the diffusion-induced material migration (DIMM). During drying, inwards diffusion of the lactose, protein and fat molecules may occur due to water evaporation. Since lactose, protein and fat have a distinct difference in hydrodynamic radius⁹, there was also a relatively great variance in the diffusivities. For a specific solid content, the component with higher size has the lower diffusivities. Based on Table 2, the diffusivity of protein is approximately one or two orders magnitudes lower than the diffusivity of lactose, while the diffusivity of fat is estimated to be three orders magnitudes lower than the diffusivity of lactose^{9, 16}. This probably made inward diffusion of the lactose the fastest among the three species which resulted in the accumulation of the lactose at the core of the droplets. As shown in Figure 2(a) and 3, as drying progressed, the surface composition of lactose decreased possibly due to the increase of the surface composition of protein as described in Figure 4. This was in line with the previous study which indicated that the surface composition of lactose was half of the bulk composition¹⁵. Figure 2(a) shows that the degree of change in surface composition decreased as drying progressed, which may be explained by the effect of decrease of diffusivity during drying. The Stokes-Einstein diffusivity predicts the diffusivity according to the molecular size and temperature. Nevertheless, more appropriate diffusivity function was proposed by Quemada³⁷ to take into account the effects of the fraction of the involving species. According to equation (B1), the function of $(1 - \phi / \phi_m)^2$ became unity for the highly diluted species and

nearly achieved zero for the very concentrated species. In line with moisture removal during drying, the fraction of lactose increased and the function of $(1 - \phi / \phi_m)^2$ decreased which lowered the diffusivity of lactose.

In agreement with the experimental data shown in Figure 2(b), the surface composition of protein increased during drying. Figure 2(b) indicates that the modelling results match the experimental data. As shown in Figure 4, although protein has higher diffusivity than fat, overrepresentation of protein at the surface was observed. The composition of protein at the outer part of the droplets was also higher than the core composition. The overrepresentation of the surface protein composition was also reported previously³⁸⁻⁴⁰. The addition of 0.5-1% of milk protein led to the overrepresentation of protein composition up to nearly 60%⁴¹. The component transport inside the droplets was not primarily governed by DIMM (refer to sensitivity analysis in Section 4.3). The overrepresentation of protein at the surface was deemed to be due to its surface activity^{17, 42}. The prominent surface activity resulted in adsorption of protein molecules at the air/water interface, which increased its surface concentration^{43, 44}. Measurement of the surface pressure also confirmed similar findings⁴⁵. During adsorption, the protein formed films which consists of irreversibly adsorbed molecules with a thickness of 50-100 Å^{43, 44}. In this study, adsorption of protein at the air/water interface was captured by the boundary condition (equation (17)). It appears that both DIMM and surface activity played an important role in determining distribution of composition of protein. Nevertheless, the surface activity may be more dominant in governing the distribution.

For the fat, the predictions of the surface composition are shown in Figure 2(c). Prior to the beginning of drying, an accumulation of fat at the surface had already existed as described by the initial surface condition, which could be because of component segregation

during droplet generation. This will be further elaborated in Section 4.4. Subsequently, although fat has the highest hydrodynamic radius, the surface composition of fat decreased during drying. This could be due to the dominant effect of the surface activity of protein. It appears that the adsorption of protein at the air/water interface was more dominant in governing the transport inside the particles than the DIMM. Furthermore, the extent of change of surface composition reduced as drying progressed which was because of a significant increase in the droplet viscosity as encapsulated in the diffusivity function (equation (B1)). During drying, due to moisture removal, the fraction of fat increased which reduced the function of $(1 - \phi/\phi_m)^2$ and thus also decreased the diffusivity of the components. It seems that since the beginning of drying, fat was located at the surface and played an important role in early shell formation. The early presence of fat at the surface may also ease the adsorption of protein at the air/water interface¹¹.

By implementing scheme 1, reasonable predictions of surface composition and component segregation inside LFME droplets have been made. The model can be used to estimate the surface properties of dairy droplets. In future, the phenomena associated with surface properties such as flowability, stickiness, crystallinity and dissolution behaviors can potentially be predicted by incorporating this model.

4.2 Modelling of component segregation during single droplet drying using the bulk composition as initial condition (scheme 2)

By using the measured initial surface composition, the model was able to describe fairly well the kinetics of surface composition and transport phenomena inside the materials undergoing single droplet drying. It will be interesting to see if the bulk composition is applicable to be implemented as the initial condition in the modelling, as often reported in

literature. If the bulk composition was able to serve as the initial conditions, it would simplify the model application since it would be unnecessary to measure the initial surface composition. It was thus attempted to employ the model (equations (1) to (17)) by using the bulk composition of lactose, protein and fat (listed in Table 1) as the initial conditions.

Figures 2(a) and Figures S3 to S5 (supplementary figure files) show the results for this scheme. As shown in Figure 2(a), for lactose, although the agreement of the surface composition value was not attained, the model estimated the general trends in component composition during drying correctly. The predicted surface composition of lactose decreased during drying in line with the experimentally measured surface composition. The composition of lactose at the core became greater than that at the outer part due to DIMM. Compared to the model implementing the measured initial surface condition as the initial conditions, however, Scheme 2 yielded less agreement with the experimental data. This was reflected by the greater predicted surface composition in lactose for Scheme 2 since the bulk composition of lactose was nearly twice as much as the measured initial surface composition. Furthermore, by using this scheme, the accumulation of fat ahead of the actual drying process was not captured. This caused the fraction of surface that in reality was initially occupied by fat to be covered by lactose instead.

For the protein, as shown in Figures 2(b) and S4 (supplementary figure file), the surface composition increased during drying in agreement with the experimental data. Benchmarks towards the results yielded by Scheme 1 indicated that Scheme 1 generated slightly closer agreement towards the experimental data. Scheme 2 resulted in lower predictions than scheme 1 which was reasonable since the bulk composition of the protein (as the initial condition) was lower than the measured initial surface composition. Compared to the discrepancy of surface

composition of lactose resulted by this scheme (as discussed above), the discrepancy of surface composition of protein was smaller which may be because the difference of bulk and measured initial surface composition was also smaller. Figure S4 (supplementary figure files) indicates that due to the surface activity of protein, the protein molecules were attracted to the air/water interface. Similar to scheme 1, the effects of surface activity were more prominent than the DIMM which led to a lower composition at the droplet core.

As indicated in Figures 2(c) and S5 (supplementary figure file), the predictions of surface composition of fat obtained with Scheme 2 were smaller than the experimental data and the modeling using Scheme 1. As highlighted above, this scheme did not incorporate the overrepresentation of fat since the beginning of drying. In this scheme, a very low bulk composition of fat (0.29 %-wt) was applied. This composition also kept decreasing during drying because of the surface activity of protein. The underestimation of surface concentration of fat during drying seems to be responsible for the overestimation of surface concentration of lactose. In addition, the internal profiles generated by this scheme (Figure S5, supplementary figure file) were different from the ones resulted from Scheme 1 (Figure 5). Here, accumulation of concentration of fat at the surface was not shown due the very low bulk composition of fat. Therefore, this scheme appears to be less realistic than Scheme 1 in yielding the component distribution inside the dried particles.

The numerical investigation of scheme 1 and 2 indicates that the bulk composition seems to be less appropriate than the measured initial surface composition to serve as the initial conditions of the model. Scheme 2 did not give the accuracy level as high as that of Scheme 1. Therefore, it is suggested that experimentally determined initial droplet surface conditions should be implemented as the initial conditions for the modelling of component distribution

during single droplet drying which can be obtained via cryogenic flash-freezing¹⁶. This further highlights the importance of application of measured initial surface composition for accurate estimations of dynamics of surface composition and properties during drying. At the moment, no instrument is commonly available to measure the initial surface composition at industrial settings. Nevertheless, recent studies^{14,16} indicated that perforation mechanisms under mechanical stress resulted in the difference between the bulk composition and experimentally determined initial surface composition. More works will be developed as the part of the predictive tools.

4.3. Sensitivity analysis of transport parameters

In order to evaluate the robustness of the model, a sensitivity analysis was undertaken on the transport parameters, i.e. the diffusivities of lactose, protein and fat as well as the kinetic parameters of protein adsorption (k_a). The sensitivity analysis was performed in the range of $\pm 20\%$ of the standard parameter values used in the model.

Figures 6(a-c) show the impacts of the sensitivity analysis for the fat diffusivity on the surface composition of fat, protein and lactose. As shown in Figure 6(a), an increase of diffusivity of fat resulted in a smaller surface composition of fat. This was reasonable since the higher diffusivity accelerated the inward diffusion which yielded less accumulation of this component at the surface. Accordingly, a greater surface composition of lactose and protein was observed at the surface as shown in Figures 6(b) and 6(c). Nevertheless, the alteration of diffusivity of fat within a 20% range only gave minor modification of the temporal profiles in surface composition of lactose, protein and fat during drying.

Unlike the diffusivity of fat, there was no noticeable difference of the change in diffusivity of lactose and protein on the profiles of surface composition of lactose, protein and fat during drying (Figures S6 (a-c) and S7 (a-c), supplementary figure files). In agreement with the above discussion, the increase of diffusivity of lactose should slightly lower the surface composition of lactose and hence slightly alter the surface composition of fat and protein. However, since the hydrodynamic radius of lactose is much smaller than that of fat, the effects of diffusivity of lactose were much less significant than those of fat. Therefore, the selection of molecular size of lactose may not be very critical in determining the profiles of surface composition. The impact of the diffusivity of protein was also small because its surface enrichment was primarily driven by the surface activity and not DIMM, as confirmed by the following sensitivity study of the influence of the surface activity of protein.

A sensitivity analysis was undertaken on the kinetic parameters of protein adsorption (k_a), whose results are shown in Figure 7 (a-c). An increase of this parameter resulted in a rise in surface composition of protein indicating that the adsorption rate at the air/water interface was enhanced. In line with this, a decrease of surface composition of lactose and fat was observed.

4.4. Investigation of the difference between the initial measured surface composition and the bulk composition prior to drying

It has been largely published that there is often found a distinct difference between bulk and surface compositions in spray-dried powders^{6-8, 14-16, 33, 46}. As listed in Table 1, prior the start of drying the initial, experimentally determined surface composition was significantly different from the bulk composition. Droplet generation may be an important factor that promoted the overrepresentation of fat. The enrichment of fat at the surface of spray-dried milk

powder after atomization may be due to the shear or extensional stress imposed by the atomizer^{14, 15}. The presence of fat globules may result in a perforation mechanism under this mechanical stress that causes a preferred emulsion break-up along the dispersed lipid phase⁴⁷. As such, the fat phase was believed to cover the surface immediately after droplet formation without the need to diffuse to there first. Considering the very short time that lapsed from commencement of droplet generation to cryogenic flash-freezing (two or three seconds) and the slow diffusivity of the fat globules, it is unlikely that the difference between surface and bulk composition was due to diffusion¹⁶.

Although experimental studies have shown the difference between the bulk composition and initial surface composition, the mechanisms underlying this have not been fully understood. More importantly, to the best of our knowledge, there has been no process simulation implemented to investigate this issue. Therefore, the modelling here was attempted to elaborate on this. It is hypothesized that diffusion was not the only factor that influenced this difference. If the initial component gradients were only due to diffusion, when implementing the bulk composition as the initial conditions, the predicted surface compositions should be similar to the measured initial surface composition within the first few simulated seconds. In order to reflect this, equations (12) to (14) were solved simultaneously in conjunction with the initial and boundary conditions (equations (15) to (17)). The bulk composition of lactose, protein and composition as listed in Table 1 was used as the initial condition. Since this simulation was aimed to observe the component migration prior to drying, equations (1) to (3) were not incorporated into the modelling.

The simulation results are shown in Figures 8 (a-c). Even after very long time (7 min), the agreement between the simulated results and the measured initial composition was not attained. More importantly, an increase of surface composition of fat, which was expected to occur during the process, was not observed. This suggested that diffusion was not the only

factor that governed the initial movement of the components inside the droplets before the drying starts. The simulation results further strengthen the arguments that the difference between the bulk and measured initial composition are due to the disintegration mechanism which immediately exposes the fat globules to the droplet surface^{6,7, 14-16, 46}.

Based on the simulation, it appears that material segregation was essentially the coupling effects of atomization, diffusion and surface activity. Initially, fat may accumulate at the surface as a result of the atomization process. During drying, the mechanisms coupled with the DIMM which influenced the component distribution according to their size.

Conclusion

The kinetics of surface composition during drying of dairy droplets containing low fat content were modelled in this study. The model combined the heat and mass transfer with a set of equations of mass conservation of lactose, protein and fat. The model was found to be accurate to describe the component migration and dynamics of surface composition during drying. Both diffusion and protein surface activity played an important role in component distribution during drying. While diffusion-induced material migration governed the component distribution of lactose and fat, the surface activity of protein was more dominant in determining the protein composition inside the droplet. The study indicated that the measured initial surface composition instead of the bulk composition should be applied as the initial conditions. The simulation further suggested that the difference between the initial surface composition and the bulk composition prior to drying may not be primarily governed by diffusion. This supported the argument that the disintegration mechanism during droplet generation was responsible for this difference. The model will pave the way for predicting quality changes induced by surface properties, including flowability, stickiness and dissolution behaviours. The model can be used

as an alternative tool in optimising drying schemes to manufacture particles with adjustable surface properties.

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Appendix. The diffusivities, shrinkage relationship and physical properties of the droplets

The diffusivity of lactose, protein and fat can be represented as^{37, 48}:

$$D_i = \frac{K_B T}{6\pi\mu(1 - \phi/\phi_m)^{-2} R_i} \quad (A1)$$

where i denotes lactose, protein or fat, D_i is the diffusivity of the components [m^2/s], R_i is the hydrodynamic radius of the components [m] (refer to Table 2), μ is viscosity [$\text{Pa}\cdot\text{s}$], T is the temperature, ϕ is the volume fraction of the components, ϕ_m is the maximum volume fraction of the components and K_B is the Stefan Boltzman constant [$=1.38 \times 10^{-23} \text{ kg}\cdot\text{m}^2/\text{s}^2/\text{K}$].

The change of droplet radius during drying can be represented as:

$$\frac{R}{R_0} = 0.0747(X - X_b) + 0.6947 \quad (A2)$$

In this study, perfect shrinkage wasnot implemented since the linear shrinkage gave better agreement towards the experimental data^{24, 49}. The good agreement between the fitted and experimental radius wasconfirmed by R^2 of 0.989.

Kinetic parameters for the adsorption of albumin at the air/water interface⁵⁰ were used to estimate the surface activity parameters of adsorption of protein (equation (15). Considering several types of protein and the dependency of parameters on initial concentration, pH and temperature⁵⁰, a sensitivity analysis was undertaken to obtain the best agreement with the experimental data. It has been found that the data was well represented by increasing the value of the adsorption parameterof albumin by 30%. This appeared reasonable since casein was reported to result in a moresignificant reduction of surface tension than albumin, which indicates that the kinetic parameters for adsorption of casein is greater than those of albumin¹³.

The thermal conductivity of water, lactose, protein and fat could be expressed as⁵¹:

$$k_{water} = 0.571 + 1.763 \times 10^{-3}(T - 273.15) - 6.7036 \times 10^{-6}(T - 273.15)^2 \quad (A3)$$

$$k_{lactose} = 0.20141 + 1.387 \times 10^{-3}(T - 273.15) - 4.3312 \times 10^{-6}(T - 273.15)^2 \quad (A4)$$

$$k_{protein} = 0.1781 + 1.196 \times 10^{-3}(T - 273.15) - 2.7178 \times 10^{-6}(T - 273.15)^2 \quad (A5)$$

$$k_{fat} = 0.1807 + 2.7604 \times 10^{-3}(T - 273.15) - 1.7749 \times 10^{-6}(T - 273.15)^2 \quad (A6)$$

where k_{water} , $k_{lactose}$, $k_{protein}$, k_{fat} are the thermal conductivities of water, lactose, protein and fat, respectively [W/m/K].

The density of water, lactose, protein and fat could be expressed as⁵¹:

$$\rho_{water} = 997.18 + 3.1439 \times 10^{-3}(T - 273.15) \quad (A7)$$

$$\rho_{lactose} = 1599.1 - 0.31046(T - 273.15) \quad (A8)$$

$$\rho_{protein} = 1329.9 - 0.5185(T - 273.15) \quad (A9)$$

$$\rho_{fat} = 925.59 - 0.4176(T - 273.15) \quad (A10)$$

where ρ_{water} , $\rho_{lactose}$, $\rho_{protein}$, ρ_{fat} are the densities of water, lactose, protein and fat, respectively [kg/m³].

